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REFINERY PROCESSES, SURVEY

Petroleum products derived from crude oil are a convenient source of energy. Since petroleum liquids are easy to handle and store, they are well suited for transportation fuels, eg, for cars and airplanes. Other refinery products include lubricants, waxes, asphalt, solvents, and specialties such as liquefied petroleum gas (LPG), hydraulic fluids (qv), and others. Petroleum is the principal raw-material source for petrochemicals such as plastics, synthetic elastomers, certain alcohols, and other important products. The various fuel and chemical markets have their own product-quality requirements and it is the function of the refining operation to separate crude and other raw materials into fractions that are then processed to meet product specifications (see Petroleum products).

Crude petroleum contains a wide range of hydrocarbons from light gases to residuum that is too heavy to distill even under vacuum. Crude oil is primarily made up of paraffins, cycloparaffins (naphthenes), and aromatic compounds in varying proportions, some sulfur compounds, a small amount of nitrogen, but no appreciable amount of oxygen or olefins.

Refining processes can be grouped into three classes: separation, usually distillation to give the desired type of compounds; conversion, usually cracking, to change molecular weight and boiling point; and upgrading, eg, hydrotreating, to meet product-quality specifications.

In general, refineries are located near a large body of water, partly to supply cooling water but also for transportation. Large refineries process about 80,000 m^3 (5×10^5 bbl) of crude per day, which corresponds to one supertanker load. Rail transportation would require 1600 tank cars per day to carry the same amount of crude.

Since the 1970s, the great increase in crude cost has been accompanied by greater emphasis on high value products at the expense of fuel products. For example, fuel oil previously used in large power plants is displaced by coal or nuclear fuel. Since 1975, no utility power plants have been built in the United States based on burning oil or gas as fuel. Increased attention to environmental aspects has led to demand for low sulfur products despite the trend toward higher sulfur crudes. Unleaded gasoline is another example of environmental concern.

Petroleum refining has shown a rapid growth and is now the largest manufacturing industry in the United States, where petroleum products amount to ca 10% of the GNP. Gasoline accounts for ca 40% of petroleum-product consumption, diesel and fuel oil for ca 20%. Imports amount to over $\$50 \times 10^9$ per year, causing a serious imbalance of foreign-trade payments as well as uncertainty of supply.

Efforts to decrease the gasoline consumption (km/L) of vehicles by reducing their size and weight have been successful. More efficient engines are in wide use, particularly diesel engines, in which the fuel is injected directly into the combustion chamber. Diesel engines have efficiencies of about 35% versus ca 25% efficiency for gasoline engines.

Refineries range in size from 1600 m^3/d (10,000 bbl/d) to over 64,000 m^3/d (4×10^5 bbl/d). Small refineries make only gasoline, diesel, and domestic heating oils. Large refineries include the manufacture of lubricating oils and greases. Refining is also the main source of raw materials for petrochemical manufacture. A large steam-cracking unit for 500,000 t/yr of ethylene may consume ca 2×10^6 t/yr of oil feed (40,000 bbl/d), which may be 10% of the crude used in very large refinery. Clearly, chemical and fuel refining operations must be carefully coordinated.

Processing Steps

Desalting. Salt and clay or other suspended solids are removed by washing with water at 65–90°C to reduce viscosity. Typical salt content of crude may be 280 g/100 m^3; desalting may remove over 90% without the loss of oil.

Distillation. The crude is separated in continuous-fractionation plate towers, as shown in Figure 1 (see Distillation). Primary distillation takes place at atmospheric pressure and the bottom temperature is limited to 370–400°C to prevent thermal cracking.

Naphtha, the fraction taken from the top, is mainly used for motor

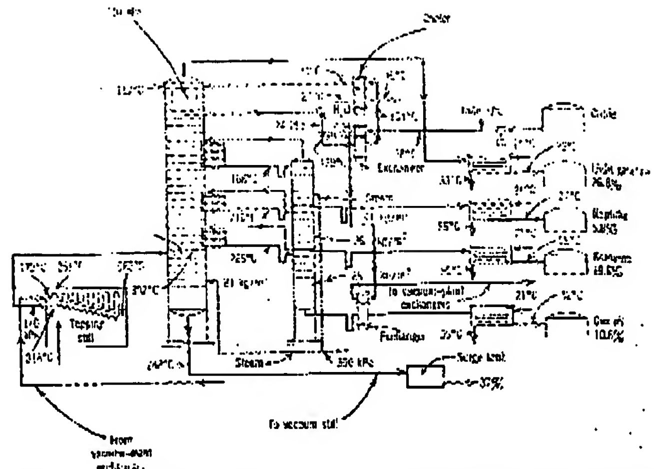

Figure 1. Atmospheric distillation of crude. Multidraw crude-oil topping plant. To convert kPa to psi, multiply by 0.145. Courtesy of McGraw-Hill Book Co., Inc.

ing oil. Kerosene and certain specialty solvents distill between these two fractions. The bottoms fraction can be used as fuel oil but is usually vacuum distilled in order to increase the yield of high value distillate oil for catalytic cracking.

Vacuum distillation provides low sulfur fuel oil by hydrosulfurizing vacuum gas oil, which is then blended back into untreated vacuum bottoms. In addition, various specialty materials are obtained, such as wax and lube fractions.

Hydroprocessing. Hydroprocessing improves the quality of various products or cracks heavy carbonaceous materials to lower-boiling, more valuable products. Mild hydrotreating removes sulfur, nitrogen, oxygen, and metals, and hydrogenates olefins. A fixed bed may be employed at 1.5–2.2 MPa (200–300 psig) and 350–400°C, without catalyst regeneration. Severe conditions are 7–21 MPa (1000–3000 psig) and 350–500°C with catalyst regeneration.

Hydrogen consumption increases with severity and depends on the amount of sulfur removed and the feed content of aromatic materials and olefins, which also consume hydrogen. Net consumption can range from 18 m^3/m^3 (100 ft^3/bbl) feed for hydrofinishing to well over 180 m^3/m^3 (1000 ft^3/bbl) feed in hydrocracking operations.

Hydrocracking. In hydrocracking, high molecular weight compounds are cracked to lower boiling materials. Severity is increased by operating at higher temperatures and longer contact time than in hydrotreating. Hydrocracking is used extensively on distillate stocks. It is of increasing importance in view of the trends to heavier crudes and the need for processing synthetic crudes.

Catalytic cracking. In catalytic cracking, heavy distillate oil is converted to lower molecular weight compounds in the boiling range of gasoline and middle distillate. Gasoline yield is high and so is the octane number. About half of the gasoline sold in the United States is obtained from petroleum by catalytic cracking, mostly by the fluidized-bed process where small particles of catalyst are suspended in upflowing gas to be handled like a liquid and circulated through pipes and valves between reaction and regeneration vessels (see Fluidization).

Catalyst circulation rates are over 50 t/min in a large plant. Temperatures range from 480–510°C in the reactor to ca 620°C in the regenerator using a synthetic silica-gel catalyst activated with 15–60% Al_2O_3. Temperatures throughout the fluidized bed vary by less than 5°C; pressures are 150–200 kPa (22–29 psi). The new zeolite catalysts can withstand higher temperatures and they are usually regenerated at 700°C. In addition, all CO is oxidized to CO_2; addition of a noble metal or other combustion catalysts in ppm concentrations assures complete combustion. With zeolite-type catalysts, 80–90% conversions are obtained. A units the